

APPLICATION FOR UNITED STATES LETTERS PATENT

For

**MODIFIED ELECTROPLATING SOLUTION COMPONENTS
IN A HIGH-ACID ELECTROLYTE SOLUTION**

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MODIFIED ELECTROPLATING SOLUTION COMPONENTS IN A HIGH-ACID ELECTROLYTE SOLUTION

FIELD

[0001] Embodiments of the invention relates generally to the field of electroplating integrated substrates and more particularly to methods for reducing defects by adjusting electroplating solution components in a high-acid electrolyte solution.

RELATED APPLICATIONS

This application is related to copending U.S. Application No. Unassigned, filed on October 8, 2003, entitled "MODIFIED ELECTROPLATING SOLUTION COMPONENTS IN A LOW-ACID ELECTROLYTE SOLUTION."

BACKGROUND

[0002] During the manufacture of integrated circuits, a semiconductor wafer is deposited with a conductive metal to provide interconnects between the integrated components. Aluminum deposition may be used for this purpose. Copper has recently been found to offer distinct advantages over aluminum as a conductive plating for an integrated circuit substrate. Copper is more conductive than aluminum and can be plated into much smaller features (e.g., trenches and vias) having high aspect ratios (e.g., greater than 4). This is an important advantage given the trend toward smaller features. Moreover, the deposition process for aluminum is more costly and complex, requiring thermal processing within a vacuum, whereas electroplating can be used to effect copper plating of semiconductor wafers.

[0003] The use of copper plating, however, is not without drawbacks. One such drawback is the problem of defects on the copper plating. These defects may take numerous forms. Two common types of defects are gap-fill defects and wetting-related defects.

[0004] Gap-fill defects include voids and seams that are the result of poor gapfill. Prior to plating, the semiconductor wafer is patterned with vias and trenches that form the interconnections; that is, vias provide the interconnection through the chip, and trenches provide the interconnections across the chip. Figure 1 illustrates the voids and seams that may occur when electroplating surfaces having small features, in accordance with the prior art. As shown in Figure 1, the substrate 100 has a number of features labeled 105A – 105D that may be trenches or vias. Voids 106, as shown in features 105A and 105C, or seams 107, as shown in features 105B and 105D, may form over the features. This problem is more pronounced for smaller features. This problem is addressed by adding a suppressant and accelerator to the electroplating solution to suppress copper plating outside the features (in the field regions 115) while accelerating copper deposition at the bottom of the features. The suppressor has relatively large molecules that cannot move into the features, whereas the accelerator has relatively small molecules that can more easily get into the features. The accelerator acts as a catalyst allowing the copper plating to grow faster from within the features, filling the features from the bottom up to avoid the formation of holes and seams in the copper plating. This solution, however, is not always effective. While the use of accelerator can reduce the occurrence of voids and seams, because the copper plating continues to grow at a faster rate over the features even after filling the features, a “hump” may be formed over the features, causing a with-in-die

WID thickness variation. WID thickness variation is the step height difference between the copper plating area over a feature region and the copper plating area over a field region.

[0005] Other types of defects include wetting-related defects and copper protrusions. Wetting-related defects include, for example, “pit” or “crater” defects, which are holes in the copper plating that extends to the seed layer. The unplated area of the wafer will be destroyed in subsequent processing, so substrates having such defects in their copper plating may be discarded. Copper protrusions are bumps resulting from high-growth copper grains in the seed layer that are replicated on the plating surface. The copper protrusions are typically 20-50 nm in diameter and protrude from the plating surface approximately 50-500 nm.

[0006] Figure 2 illustrates a typical electroplating solution in accordance with the prior art. As shown in Figure 2, the electroplating solution has a number of inorganic components (e.g., acid, copper, and chloride) and a number of organic components (e.g., accelerator, leveler, and suppressor). This typical prior solution is known as a high-acid electrolyte solution by comparison to more recent solutions that use considerably less acid. Generally a high-acid electroplating solution has a sulfuric acid concentration greater than 20 grams per liter (g/l) and more typically about 175 g/l. The various components and concentrations for the solution were developed over time for various electroplating processes. With the continuing trend toward smaller feature size and higher aspect ratios, the concentrations of various components of the prior art electroplating solution may not be ideal for such applications.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The invention may be best understood by referring to the following description and accompanying drawings that are used to illustrate embodiments of the invention. In the drawings:

[0008] Figure 1 illustrates the voids and seams that may occur when electroplating surfaces having small features, in accordance with the prior art;

[0009] Figure 2 illustrates a typical high-acid electroplating solution in accordance with the prior art;

[0010] Figures 3A – 3C illustrate the relationship between suppressor concentration and the occurrence of various defects in the electroplating in accordance with one embodiment of the invention;

[0011] Figure 4 illustrates a process in which component concentrations for a high-acid electroplating solution are determined in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION

[0012] Embodiments of the invention provide methods for reducing electroplating defects by varying the concentration of components in a high-acid electroplating solution. For one embodiment, the concentration of suppressant is increased resulting in a decrease in protrusions and wetting-related defects. In an alternative embodiment the concentrations of suppressant is increased while the concentration of chloride is decreased to reduce defects. Various alternative embodiments include an increased concentration of suppressant, a decreased concentration of chloride, together with varying concentrations of leveler and accelerator and other portions of the electroplating process to further reduce defects. In still other embodiments, the concentrations of suppressant and chloride are increased resulting in better gap-fill.

[0013] In the following description, numerous specific details are set forth. However, it is understood that embodiments of the invention may be practiced without these specific details. In other instances, well-known circuits, structures and techniques have not been shown in detail in order not to obscure the understanding of this description.

[0014] Reference throughout the specification to “one embodiment” or “an embodiment” means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, the appearance of the phrases “in one embodiment” or “in an embodiment” in various places throughout the specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more embodiments.

[0015] Moreover, inventive aspects lie in less than all features of a single disclosed embodiment. Thus, the claims following the Detailed Description are hereby expressly incorporated into this Detailed Description, with each claim standing on its own as a separate embodiment of this invention.

SUPPRESSOR

[0016] As discussed above, the prior art electroplating solution includes a suppressor concentration of approximately 3.3 milliliters per liter (ml/l). The suppressor is used in gap fill in conjunction with the accelerator to accelerate copper deposition at the bottom of the features while suppressing copper plating at the top corner of the features. The suppressor also acts as a surfactant to lower the surface tension and provide better electroplating.

[0017] Figures 3A – 3C illustrate the relationship between suppressor concentration and the occurrence of various defects in the electroplating in accordance with one embodiment of the invention. As shown in Figure 3A, the average number of bare test wafer (BTW) defects is reduced from approximately 1500 using a suppressor concentration of 3.3 ml/l to approximately 360 using a suppressor concentration of 20 ml/l. As shown in Figure 3B, the average number of protrusion defects is reduced from approximately 50 using a suppressor concentration of 3.3 ml/l to approximately 20 using a suppressor concentration of 20 ml/l. As shown in Figure 3C, the average number of pit defects is reduced from approximately 3 using a suppressor concentration of 3.3 ml/l to approximately 1 using a suppressor concentration of 20 ml/l.

[0018] Figures 3A – 3C illustrate that increasing the concentration of suppressor reduces the occurrence of various defects. However, the suppressor concentration cannot

be increased beyond a certain point without causing increased gap fill problems due to an over abundance of carbon in the electroplating solution. For example, increasing suppressor substantially above 30 ml/l in a high-acid electroplating solution results in an increase in voids.

CHLORIDE

[0019] Chloride is typically added to the electroplating solution to act as a catalyst for the suppressor and increase the conductivity of the solution. This implies that an increase in suppressor concentration should be accompanied by an increase in chloride concentration. If there is not a sufficient amount of chloride in the electroplating solution, the suppressor will not suppress copper plating effectively resulting in voids and seams as discussed above. However, experimentally it is determined that a reduced concentration of chloride, together with an increased concentration of suppressor substantially reduces defects. Therefore it is beneficial to reduce the chloride concentration to reduce defects, provided the concentration of chloride is still sufficient to promote adequate suppression for purposes of gap-fill. Electroplating solutions with a chloride concentration much above the prior art concentration of 50 mg/l (e.g., above 65 mg/l) result in a substantial increase in defects, while chloride concentrations below 30 mg/l may result in poor gap.

LEVELER

[0020] The prior art electroplating solution also typically includes a leveler concentration of approximately 8 ml/l. In the prior art electroplating solution, leveler serves to reduce stress-related voiding defects. The prior art concentration of leveler (i.e., 8 ml/l) has no discernible effect upon WID thickness variation. Experimentally,

increased leveler concentration of from 12 – 15 ml/l reduces the WID thickness variation. However in a high-acid electroplating solution with an increased suppressor concentration, an increase in leveler results in an increase in defects.

ACCELERATOR

[0021] Typical prior art electroplating solutions include an accelerator concentration of approximately 1.5 ml/l. For high-acid electroplating solutions in which the chloride is increased (e.g., to improve gap fill), a slight increase in accelerator is found, experimentally, to decrease defects. In one embodiment, an accelerator concentration in the range of 1.5 ml/l – 3.3 ml/l is used to decrease defects for a high acid electroplating solution having a chloride concentration higher than 30 mg/l.

[0022] Slightly increasing the accelerator concentration as described above will also result in decreased defects for a high-acid solution having an increased leveler concentration (e.g., to decrease WID thickness variation). In one embodiment, an accelerator concentration in the range of 1.5 ml/l – 3.3 ml/l is used to decrease defects for a high acid electroplating solution having a leveler concentration higher than 4 ml/l.

[0023] The increased accelerator concentration is also found to reduce defects in high-acid electroplating solutions having both increased chloride and leveler concentrations.

[0024] Figure 4 illustrates a process in which component concentrations for a high-acid electroplating solution are determined in accordance with one embodiment of the present invention. Process 400, shown in Figure 4, begins at operation 405 in which the concentration of suppressor is determined. In general, increased suppressor concentration decreases defects provided the concentration is not so high as to result in poor gap fill as

described above. In accordance with one embodiment of the invention the suppressor concentration is determined to be greater than 3.3 ml/l. For one embodiment the suppressor concentration is approximately 20 ml/l. For one embodiment the suppressor concentration is limited by poor gap fill (occurrence of voids and seams) resulting from an excess of carbon in the solution. That is, the suppressor concentration is determined as a maximum that will still effecting proper (acceptable) gap-fill.

[0025] At operation 410 the chloride concentration is determined. The chloride concentration is kept as low as possible (to reduce defects) while maintained sufficiently high to provide proper gap fill (reduce the occurrence of void and seam defects). That is, the chloride concentration is determined as a minimum that will still effecting acceptable gap-fill. For one embodiment, the feature size and aspect ratio are considered in determining the chloride concentration. That is, because larger feature sizes require less active suppression of the copper plating, the chloride concentration can be lower for larger feature sizes and/or features having lower aspect ratios. For one embodiment, for an electroplating process to electroplate wafers having sub-0.1 um features with high (8 or higher) aspect ratios, the chloride concentration is determined to be greater than 30 mg/l, to ensure proper gap fill. For such an embodiment the chloride concentration is preferably less than 65 mg/l.

[0026] At operation 415, the concentration of leveler is determined. In accordance with one embodiment of the invention the leveler concentration is determined by evaluating the benefits of reducing WID thickness variation with the detriment of increased defects. For one embodiment, the leveler concentration is determined to be within the range of 8-12 ml/l.

[0027] At operation 420 the concentration of accelerator is determined. For one embodiment the concentrations of chloride and leveler are considered in determining the concentration of accelerator. For one embodiment if the chloride concentration is above 30 g/ml or the leveler concentration is above 4 ml/l, the accelerator concentration is determined to be above 1.5 ml/l. For one such embodiment, the accelerator concentration is determined to be approximately 3.3 ml/l.

[0028] It will be appreciated that embodiments of the invention may consist of less than all of the operations of process 400. For example, one embodiment of the invention consists in determining an increased level of suppressor to reduce defects.

GENERAL MATTERS

[0029] Embodiments of the present invention Embodiments of the invention provide methods for reducing electroplating defects by varying the concentration of suppressor and chloride components in a high-acid electroplating solution. In one embodiment the feature size may be considered in determining such concentrations. While embodiments of the invention have been described as applicable to wafers having relatively small feature sizes (i.e., less than 0.1um), alternative embodiments of the invention are applicable to other feature sizes, larger or smaller. For example, wafers having larger features but, with relatively high aspect ratios, would benefit from embodiments of the invention.

[0030] Moreover, embodiments of the invention have been described in reference to an electroplating process using a copper electroplate and a silicon wafer. In alternative embodiments, the wafer could be any suitable material, including semiconductors and

ceramics. Likewise, the electroplate may be any suitable material, including alloys of copper and silver or gold, or multilayers of such materials.

[0031] While the invention has been described in terms of several embodiments, those skilled in the art will recognize that the invention is not limited to the embodiments described, but can be practiced with modification and alteration within the spirit and scope of the appended claims. The description is thus to be regarded as illustrative instead of limiting.